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Systematic behaviour of electron redistribution on formation of halogen-bonded complexes $B\cdots XY$, as determined via XY halogen nuclear quadrupole coupling constants

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Abstract

Equilibrium nuclear quadrupole coupling constants associated with the di-halogen molecule XY in each of 60 complexes $B\cdots XY$ (where B is one of the Lewis bases N_2 , CO , HCN , H_2O , H_2S , $HCCH$, C_2H_4 , PH_3 , NH_3 or $(CH_3)_3N$ and XY is one of the di-halogens Cl_2 , $BrCl$, Br_2 , ICl , IBr or I_2) have been calculated *ab initio*. The Townes-Dailey model for interpreting the changes in the coupling constants when XY enters the complex was used to describe the electron redistribution in the di-halogen molecule in terms of the fraction δ_i of an electron transferred from the Lewis base B to atom X and the fraction δ_p of an electron transferred simultaneously from atom X to atom Y . Systematic relationships between the δ_i values for the six series are established. It is shown that, in reasonable approximation, δ_i decays exponentially as the first ionisation energy I_B of the Lewis base B increases, that is $\delta_i = A \exp(-b I_B)$. It is concluded from the results for the series $B\cdots BrCl$, $B\cdots Br_2$, $B\cdots ICl$, $B\cdots IBr$ and $B\cdots I_2$ that the coefficients A and b in regression fits to the corresponding logarithmic version $\ln(\delta_i) = \ln(A) - b(I_B)$ of the equation are not strongly dependent on either the halogen atom X directly involved in the halogen bond in $B\cdots XY$ or, for a given X , on the nature of Y . The behaviour of PH_3 as a Lewis base appears to be anomalous. Values of δ_i and δ_p calculated by the quantum theory of atoms-in-molecules and natural bond orbital methodologies give results very close to those from application of the Townes-Dailey approach described.

1. Introduction

The halogen bond refers to the non-covalent, attractive interaction of an electrophilic region associated with a halogen atom in a molecule and a nucleophilic region (for example, a non-bonding or a π bonding electron pair) of another, or the same, molecule and was defined by a IUPAC Working Party in 2013[1]. The numbers of publications concerned with the halogen bond have grown very rapidly since the late 1990's, as described in a recent comprehensive review [2], which also gives a detailed history of the discovery and development of this non-covalent interaction. The halogen bond was recognised as largely electrostatic in origin through a comparison of several properties of isolated halogen-bonded complexes $B\cdots XY$, (where B is a Lewis base and XY is a dihalogen molecule) with those of isolated hydrogen bonded complexes $B\cdots HX$, as investigated by rotational spectroscopy, that is the halogen bond energy arises mainly from the interaction of unperturbed electric charge distributions of the interacting molecules [3]. The electrophilic site associated with a halogen atom that can form a halogen bond has been described in terms of a σ -hole [4,5], that is a region of depleted electron density and relatively positive electrostatic potential opposite the bond in, for example, Cl_2 .

The interaction of two molecules to form a complex can never be entirely electrostatic in the sense defined above, however, because the electric charge distribution of the one component of the complex polarises the electric charge distribution of the other and *vice versa*. There has been some discussion about whether 'charge transfer' is a phenomenon that is different from polarisation [6,7]. Some years ago, in connection with the experimental investigation of halogen-bonded complexes in isolation in the gas phase, it was recognised that halogen-bonded complexes of the type $B\cdots XY$ carry information about the electric charge redistribution that accompanies their formation [8-12]. This information is available through the changes in the nuclear quadrupole coupling constants of the atoms X and Y when the XY molecule is subsumed into the complex. Unfortunately, only zero-point coupling constants are presently available from the rotational spectra of $B\cdots XY$ and, consequently, the way they change due to electric charge redistribution is mixed up with changes brought about by the zero-point oscillations of the two components of the weakly bound complex. No entirely satisfactory method has been discovered for the deconvolution of these two effects, but calculation of nuclear quadrupole coupling constants *ab initio* leads straight-forwardly to equilibrium values, which do not suffer from zero-point effects.

In this article, we present the equilibrium halogen nuclear quadrupole coupling constants calculated *ab initio* for 60 halogen-bonded complexes $B\cdots XY$, where B is one of the ten simple Lewis bases N_2 , CO, HCN, H_2O , H_2S , HCCH, C_2H_4 , PH_3 , NH_3 or $(CH_3)_3N$ and XY is one of the six di-halogen molecules Cl_2 , BrCl, Br_2 , ICl, IBr or I_2 . We then interpret these coupling constants to yield information about two properties that result from the mutual polarisation of B and XY, namely the changes in the electronic populations at both X and Y when the complex is formed.

2 Theoretical Methods

2.1 *Ab initio* calculations of geometries and nuclear quadrupole coupling constants of molecules XY and $B\cdots XY$

The geometry of each $B\cdots XY$ system investigated here was optimized at the MP2/aug-cc-pVTZ computational level [13,14]. For complexes $B\cdots XY$ in which iodine atoms are present, the aug-cc-pVTZ-PP basis set was used for those atoms. Frequency calculations were carried out to confirm that the geometries obtained corresponds to energy minima, except for the complexes in which $(CH_3)_3N$ was the Lewis base, in which cases it was assumed that the minima correspond to molecules of C_{3v} symmetry. The calculation of the nuclear quadrupole coupling constants was conducted at the MP2/aug-cc-pV5Z level of theory in the geometries obtained at MP2/aug-cc-pVTZ level. In order to obtain the corresponding constants for the complexes that include iodine atoms, the full electron AQZP basis set [15] has been used for these atoms. All *ab initio* calculations were carried out with the Gaussian-16 program [16].

In addition, the δ_i and δ_p values (the fractions of an electronic charge polarized from B to X and from X to Y, respectively) have been derived from the charges obtained by integration of the electron density at the atomic basins within the quantum theory of atom in molecules [17,18] methodology at the MP2/aug-cc-pVTZ computational method and the AIMAll program [19]. In all cases, the integrated atomic Laplacian values have been used as a measure of the quality of the integration [20]. For completeness, δ_i and δ_p were also computed by the natural bond orbital (NBO) methodology [21] with the NBO-6 program [22].

2.2 Calculation of electron redistribution in XY on formation of B...XY: The Townes-Dailey model

The nuclear spin angular momentum I_X associated with a nucleus X in a di-halogen molecule XY can couple to the overall rotational angular momentum J of the molecule by virtue of the electrostatic interaction of a non-zero nuclear electric quadrupole moment Q_X of nucleus X with the electric field gradient $q_{zz} = \partial^2 V^X / \partial z^2$ at the X nucleus along the intermolecular axis direction z of XY. Only a limited number of orientations of the X nuclear spin axis with respect to z are allowed and each of these corresponds to a different energy of interaction of Q_X with $\partial^2 V^X / \partial z^2$. Similar arguments apply if Q_Y of nucleus Y is also non-zero. The result is a splitting of the rotational energy levels and transitions of XY into so-called nuclear quadrupole hyperfine components, the measurement and analysis of which leads to nuclear quadrupole coupling constants $\chi_{zz}(X)$ and $\chi_{zz}(Y)$ defined by

$$\chi_{zz}(X) = eQ_X (\partial^2 V^X / \partial z^2) \quad (1)$$

$$\chi_{zz}(Y) = eQ_Y (\partial^2 V^Y / \partial z^2) \quad (2)$$

In eqns. (1) and (2), e is the protonic charge and Q_X and Q_Y are the conventional nuclear electric quadrupole moments, all of which are known constants. Thus, eqs. (1) and (2) provide routes to the electric field gradients (efgs) at X and Y along the axis z of the diatomic molecule XY. The efg at a given nucleus X arises entirely from the electric charge distribution in the molecule XY that is outside nucleus X.

Townes and Dailey [23,24] introduced a simple model for interpreting nuclear quadrupole coupling constants that can yield information about the electron distribution within the molecule XY in reasonable approximation. The model assumes that filled electron shells associated with an atom X remain spherically symmetric when X enters the molecule XY and therefore that the efg at the X nucleus along the XY internuclear axis z arising from such shells can be neglected. Thus, only valence-shell electrons need be considered. Moreover, the contribution to $q_{zz} = \partial^2 V^X / \partial z^2$ from valence-shell electrons centred on atom Y are neglected because the efg at a nucleus arising from a given electron varies with the distance r of that electron from the nucleus according to $\langle r^{-3} \rangle$. Valence shell ns electrons are assumed to retain their spherical symmetry when X enters the XY molecule. Hence, only np , nd , valence electrons centred on X can contribute significantly to $\partial^2 V^X / \partial z^2$ in this model. Further, such orbitals are assumed

to be unperturbed from those of the free atom. Writing $q_{n,l,m}$ as the efg arising from a single $np_{l,m}$ electron in the free atom X, it follows that the efg along the z direction at the nucleus of the halogen atom X having electronic configuration np^5 in the molecule XY is just $2q_{n,l,1} + 2q_{n,l,-1} + q_{n,l,0} = -q_{n,l,0}$, when the equality $q_{n,l,1} + q_{n,l,-1} + q_{n,l,0} = 0$ required by the spherical symmetry of a half-filled np shell is employed. Defining the nuclear quadrupole coupling constant of the free atom X as $\chi^A(X) = -eQ_X q_{n,l,0}^X$, that is the coupling constant arising from the absence of a np_z electron, it follows that, in the approximation of the Townes-Dailey model, the coupling constant of X when in the free XY molecule is just $\chi_{zz}^{\text{free}}(X) = -eQ_X q_{n,l,0}^X = \chi^A(X)$, with a corresponding expression for $\chi_{zz}^{\text{free}}(Y)$. Accurate values of $\chi^A(X)$ and $\chi^A(Y)$ are available from atomic spectroscopy [24] for the three halogen atoms considered here. This model therefore implies a value of $\chi_{zz}^{\text{free}}(\text{Cl}_2) = \chi^A(\text{Cl}) = -109.74$ MHz [24] for $^{35}\text{Cl}_2$, which is in good agreement with -111.720 MHz deduced experimentally by Gerry and co-workers [25] from a study of $\text{Ar}\cdots\text{Cl}_2$. In the case of heteronuclear di-halogen molecules, such as BrCl , $\chi_{zz}^{\text{free}}(\text{Br})$ and $\chi_{zz}^{\text{free}}(\text{Cl})$ can no longer be equated to $\chi^A(\text{Br})$ and $\chi^A(\text{Cl})$, respectively, because of a significant contribution of the ionic structure $\text{Br}^+\cdots\text{Cl}^-$ to the valence bond description of the molecule, estimated to be 6 % in ref.[24],

When $\text{B}\cdots\text{XY}$ is formed by bringing up the Lewis base B to XY along the internuclear axis z of XY, the efgs at X and Y (and hence the nuclear quadrupole coupling constants) change as a result of the effect of the electric field and its gradients arising from the electric charge distribution that is B. The complete way to evaluate these effects is to calculate the electric field and its gradients due to B at the position occupied by XY and then to calculate the changes in efg at the nuclei X and Y by using the corresponding response tensors associated with the XY charge distribution [9,10], but this is a complicated process that requires accurate values of all the quantities involved. A simpler, approximate approach [8-12] assumes that the efg changes can be modelled in terms of a fraction δ_i of an electron polarised from B into the np_z orbital of X and, simultaneously, a fraction δ_p of an electron polarised from X into the $np_{l,m}$ orbital of Y. It then follows [12] from application of the Townes-Dailey model that the nuclear quadrupole coupling constants in the equilibrium geometry of the complex $\text{B}\cdots\text{XY}$ are given by

$$\chi_{zz}^{\text{complex}}(X) = \chi_{zz}^{\text{free}}(X) - (\delta_i - \delta_p)\chi^A(X) \quad (3)$$

and

$$\chi_{zz}^{\text{complex}}(\text{Y}) = \chi_{zz}^{\text{free}}(\text{Y}) - \delta_{\text{p}}\chi^{\text{A}}(\text{Y}) \quad (4)$$

In eq.(3) and (4), $\chi_{zz}^{\text{free}}(\text{X})$ and $\chi_{zz}^{\text{free}}(\text{Y})$ are the equilibrium coupling constants of the free molecule XY. As described in Section 2.1, equilibrium nuclear quadrupole coupling constants for all 60 B...XY and the six free di-halogen molecules Cl₂, BrCl, Br₂, ICl, IBr and I₂ have been calculated *ab initio* and these will be used in Section 3.1 to provide a route to values of δ_{i} and δ_{p} .

3. Results

3.1 Calculated equilibrium nuclear quadrupole coupling constants

The two *ab initio*-calculated, equilibrium nuclear quadrupole coupling constants $\chi_{zz}^{\text{complex}}(\text{X})$ and $\chi_{zz}^{\text{complex}}(\text{Y})$ for the each complexes B...XY, where B is one of the Lewis bases N₂, CO, HCN, H₂O, H₂S, HCCH, C₂H₄, PH₃, NH₃ or (CH₃)₃N and XY is one of the di-halogen molecules Cl₂, BrCl, Br₂, ICl, IBr or I₂, are set out in Tables 1 and 2. The levels of theory used for the various di-halogen molecules are described in Section 2.1. Edited versions of outputs containing the optimised geometries (as cartesian coordinates) of all complexes B...XY are available as Supplementary Information. As examples of the optimised geometries, those for B...BrCl are shown, drawn to scale, in Figure 1. In all cases except when B = H₂O or H₂S, the B...XY molecules belong to one of the point groups C_{nV} ($n = 2, 3$ or ∞) and the principal inertia axis *a* of the complex coincides with the axis *z* of the diatomic molecule. Consequently, there are no off-diagonal elements of the equilibrium coupling tensors $\chi_{\alpha\beta}^{\text{complex}}(\text{X})$ and $\chi_{\alpha\beta}^{\text{complex}}(\text{Y})$, where α and β are to be permuted over the principal inertia axes *a*, *b* and *c*. (See Supplementary Information for the complete coupling tensors) The complexes H₂O...XY and H₂S...XY, however, have *C_s* symmetry (see Figure 1) and therefore the coupling tensors in their principal inertia axis systems have small, non-zero off-diagonal elements $\chi_{ac}^{\text{complex}}(\text{X})$ and $\chi_{ac}^{\text{complex}}(\text{Y})$. The full coupling tensors $\chi_{\alpha\beta}^{\text{complex}}(\text{X})$ and $\chi_{\alpha\beta}^{\text{complex}}(\text{Y})$ for such molecules were therefore diagonalized to yield the required values of $\chi_{zz}^{\text{complex}}(\text{X})$ and $\chi_{zz}^{\text{complex}}(\text{Y})$, as given in Table 1. The values of $\chi_{zz}^{\text{free}}(\text{X})$ and $\chi_{zz}^{\text{free}}(\text{Y})$ along the *z*-axis of the free di-halogen molecules Cl₂, BrCl, Br₂, ICl, IBr or I₂, as calculated at the level of theory used for their corresponding complexes B...XY (see Section 2.1), are recorded in Table 3.

3.2 Calculated values of δ_i and δ_p

In the approximation of the Townes-Dailey model for interpreting nuclear quadrupole coupling constants, it was shown in Section 2 that, when a complex $B \cdots XY$ is formed from B and XY, the accompanying electron redistribution can be simply related via eqs. (3) and (4) to the equilibrium nuclear quadrupole coupling constants $\chi_{zz}^{\text{complex}}(X)$ and $\chi_{zz}^{\text{complex}}(Y)$ of the complex $B \cdots XY$, those $\chi_{zz}^{\text{free}}(X)$ and $\chi_{zz}^{\text{free}}(Y)$ of the free XY molecules referred to the internuclear axis z , and those $\chi^A(X)$ and $\chi^A(Y)$ of the isolated halogen atoms X and Y. Rearranging eq.(3) and (4) gives the fraction δ_i of an electron transferred from the non-bonding electron pair of the Lewis base $B = N_2, CO, HCN, H_2O, H_2S, PH_3, NH_3$ or $(CH_3)_3N$ (or from the π -bonding pair when $B =$ ethene or ethyne) as

$$\delta_i = \frac{\chi_{zz}^{\text{free}}(X) - \chi_{zz}^{\text{complex}}(X)}{\chi^A(X)} + \frac{\chi_{zz}^{\text{free}}(Y) - \chi_{zz}^{\text{complex}}(Y)}{\chi^A(Y)} \quad (5)$$

while the fraction δ_p of an electron simultaneously transferred from X to Y is simply

$$\delta_p = \frac{\chi_{zz}^{\text{free}}(Y) - \chi_{zz}^{\text{complex}}(Y)}{\chi^A(Y)} \quad (6)$$

Values of δ_i and δ_p calculated with the aid of eq.(5) and (6) are set out in Table 4. The required free XY molecule and isolated atom coupling constants, $\chi_{zz}^{\text{free}}(X)$ and $\chi_{zz}^{\text{free}}(Y)$ and $\chi^A(X)$ and $\chi^A(Y)$, respectively, are in Table 3 for the various XY molecules and X and Y atoms. The atomic constants have been taken from ref.[26] .

It is possible to establish graphically that there is a systematic relationship between the δ_i values for the various $B \cdots XY$, as illustrated in Figures 2 and 3. In Figure 2, $\delta_i(B \cdots Br_2)$ is the abscissa and $\delta_i(B \cdots Cl_2)$ or $\delta_i(B \cdots I_2)$ are plotted as the ordinate for the 10 Lewis bases B considered. Each series in Figure 2 involves a non-polar halogen molecule. We note that the points lie on reasonable straight lines through the origin if the points for $H_3P \cdots Cl_2$ and $(CH_3)_3N \cdots Cl_2$ are not included in the linear regression fit for the $B \cdots Cl_2$ series. Arguments set out with reference to Figure 3 below show that the $H_3P \cdots XY$ values are anomalous, while the δ_i value of $(CH_3)_3N \cdots Cl_2$ is far too large; in fact it is larger than that of any other $(CH_3)_3N \cdots XY$ complex. In Figure 3, the values of $\delta_i(B \cdots BrCl)$ are plotted on the abscissa while those for the remaining $B \cdots XY$ ($XY = Cl_2, Br_2, I_2, ICl$ and IBr) are on the ordinate. The points for all PH_3 complexes (enclosed in the rectangular box) were not included in the linear regression fits to yield the solid straight lines since they are clearly not well-behaved. The point for $(CH_3)_3N \cdots Cl_2$ (in square box)

was again excluded from the regression fit for the $B\cdots Cl_2$ series. A systematic relationship is again noted among the linear regression lines for the various series. Moreover, it is clear from Figure 3 that the δ_i values for the three series $B\cdots IY$ ($Y = Cl, Br$ or I), in each of which an iodine atom is directly involved in the halogen bond, are very similar. This is also true for the two series $B\cdots Br_2$ and $B\cdots BrCl$ (Figure 2) but the values for the $B\cdots Cl_2$ series appear significantly lower.

Having established systematic behaviour among δ_i values of most of the 60 $B\cdots XY$ complexes investigated here, it is worth enquiring whether these quantities are related to a particular property of the Lewis bases B . If δ_i is a reasonable approximation to the fraction of an electron polarised from the non-bonding electron pair of B (or the π -electron pair when B is ethyne or ethene) onto the electrophilic region of atom X when $B\cdots XY$ is formed, it seems reasonable that the smaller is the appropriate ionisation potential I_B of B , the larger should be δ_i . When the δ_i are calculated from equilibrium nuclear quadrupole coupling constants given in Table 4, the plot of δ_i versus I_B for the series of the 30 complexes $B\cdots ICl$, $B\cdots IBr$ and $B\cdots I_2$ shown in Figure 4 results. Values of the experimental adiabatic ionisation energies I_B are taken from the NIST Computational Chemistry Comparison and Benchmark Database [27]. It is evident from Figure 4 that δ_i decreases exponentially as I_B increases. The points, with the exclusion of the three for PH_3 , were fitted by linear regression to the exponential decay $\delta_i = A\exp(-bI_B)$, which is shown as the solid black line and for which the coefficients are $A = 5.0(10)$ and $b = 0.387(22) \text{ (eV)}^{-1}$, with $R^2 = 0.944$. The justification for excluding the points for PH_3 from the fit was given earlier. Possible causes for the anomalous behaviour of PH_3 are discussed later (Section 4). Similar systematic behaviour among the corresponding values of δ_p (see Tables 1 and 2) is less clear. They too decay in a roughly exponential manner as the ionisation energy I_B of the Lewis base increases, but presumably δ_p depends not only on I_B but also on the axial polarizability of the di-halogen XY . The δ_p behaviour will be considered no further here.

It would be better to use accurate equilibrium nuclear quadrupole coupling constants determined by rotational spectroscopy in eqs, (5) and (6) to obtain δ_i and δ_p . Unfortunately, only zero-point coupling constants are available for all complexes $B\cdots XY$ so far investigated by rotational spectroscopy. If zero-point coupling constants are employed, it is necessary to modify eqs.(5) and (6) to allow for the fact that the B and XY subunits, when within the isolated complex, undergo zero-point vibrations. The angular oscillations of B and XY with respect to their centres of mass are particularly important in describing the zero-point motion of weakly bound $B\cdots XY$. Those of XY , but not B , were allowed for empirically when

zero-point coupling constants were used. The results [28] showed a similar exponential decay of δ_i with I_B , but the numerical values of δ_i were generally smaller than those calculated here from equilibrium coupling constants, presumably because the zero-point oscillations of XY were underestimated and those of B tend to reduce the average efg at points remote from B.

If the dependence of δ_i on I_B is an exponential decay, an alternative way to examine the data is to plot $\ln(\delta_i)$ against I_B . The result should then be a straight line of slope $-b$ and the value of I_B when $\ln(\delta_i) = 0$ is the ionisation energy of a hypothetical Lewis base for which $\delta_i = 1$, that is the energy for complete removal of an electron of B to the X atom of XY. The result of this approach for the data used in Figure 4 is shown in Figure 5. The points for B = PH₃ were again excluded. The remaining points lie on a reasonably good straight line as shown by the linear regression, which yields the equation $\ln(\delta_i) = 1.67(33) - 0.393(27)(I_B/\text{eV})$, with $R^2 = 0.894$. It therefore appears that, in good approximation, a single straight line is sufficient to describe the relationship between $\ln(\delta_i)$ and I_B for the 27 of complexes B...IY having B is N₂, CO, HCN, H₂O, H₂S, HCCH, C₂H₄, NH₃ or (CH₃)₃N and Y = Cl, Br or I. This suggests that it is the iodine atom involved in the halogen bond that predominates in determining δ_i , which is largely independent of atom Y.

The weak effect of the terminal atom Y can be tested further by considering the two series of complexes B...BrCl and B...Br₂, in both of which Br is the atom directly involved in the halogen bond to B while the terminal atoms are different. Figure 6 carries a plot of $\ln(\delta_i)$ against I_B for 18 complexes B...BrCl and B...Br₂, again with the two complexes having PH₃ as the Lewis base omitted. The solid line is the linear regression fit for the 18 points, described by the equation $\ln(\delta_i) = 1.30(30) - 0.350(26)(I_B/\text{eV})$ ($R^2 = 0.924$) which, within the fairly large errors, is identical with that determined for the points plotted in Figure 5. It thus appears that the difference caused by replacing the halogen bonding atom I by Br is not very significant. In fact, when the 45 B...XY complexes having XY = BrCl, Br₂, ICl, IBr and I₂, that is involving all Lewis bases apart from B = PH₃, are treated in a similar manner, the result is as shown in Figure S1 of the Supplementary Information, with the linear regression equation $\ln(\delta_i) = 1.52(23) - 0.376(20)(I_B/\text{eV})$ ($R^2 = 0.895$). The points when $\ln(\delta_i)$ is plotted against I_B for the B...Cl₂ series, as in Figure 7, seem to lie on a reasonable straight line if that for (CH₃)₃N is excluded. They yield the linear regression equation $\ln(\delta_i) = -0.37(38) - 0.267(32)(I_B/\text{eV})$ ($R^2 = 0.910$). Thus, it appears that the coefficient $-b$ of I_B is sensibly constant at ~ 0.38 eV, whether the halogen atom involved in the halogen bond is Br in BrCl or Br₂, or I in ICl, IBr or I₂. Only in the case of XY = Cl₂ does this coefficient seem

differ significantly, as is demonstrated by Table 5, in which the coefficients in the linear regression fits of the $\ln(\delta_i)$ versus I_B plots for all six individual series $B\cdots Cl_2$, $B\cdots BrCl$, $B\cdots Br_2$, $B\cdots ICl$, $B\cdots IBr$ and $B\cdots I_2$ are set out.

4. Conclusions and Discussion

The two equilibrium nuclear quadrupole coupling constants of the di-halogen molecule XY in each of 60 complexes $B\cdots XY$ (where B is one of the Lewis bases N_2 , CO, HCN, H_2O , H_2S , HCCH, C_2H_4 , PH_3 , NH_3 or $(CH_3)_3N$ and XY is one of the di-halogen molecules Cl_2 , $BrCl$, Br_2 , ICl , IBr or I_2) have been calculated *ab initio*. By using the Townes-Dailey model for interpreting the changes in these coupling constants when XY is subsumed into each complex, it has been possible to describe the electron redistribution in the di-halogen molecule in terms of the fraction δ_i of an electron transferred from the Lewis base B to atom X and the fraction δ_p of the electron transferred simultaneously from atom X to atom Y. It has been shown from graphs of $\delta_i(B\cdots XY)$ versus $\delta_i(B\cdots X'Y')$ that there is a systematic relationship between the δ_i values among the various series $B\cdots Cl_2$, $B\cdots BrCl$, $B\cdots Br_2$, $B\cdots ICl$, $B\cdots IBr$ and $B\cdots I_2$, with the exception of $B = (CH_3)_3N$ for $XY = Cl_2$ and $B = PH_3$ in the case of **the other** XY. A possible explanation for the first exception is the conclusion from a study of the rotational spectrum of $(CH_3)_3N\cdots ClF$ [29] that a significant contribution from the valence bond structure $(CH_3)_3NCl^+ \cdots F^-$ needs to be invoked to explain the observations. This conclusion was based on a large decrease in the magnitude of the ^{14}N -nitrogen nuclear quadrupole coupling constant on complex formation and we note a similar decrease (from -5.319 to -2.770 MHz) occurs for $(CH_3)_3N\cdots Cl_2$ according to the present study. Likewise, *ab initio* calculations [30] suggest a significant contribution of the valence-bond structure $H_3PCl^+ \cdots F^-$ in the complex $H_3P\cdots ClF$.

Calculation of δ_i and δ_p from the charges obtained by integration of the electron density at the atomic basins within the QTAIM methodology [17, 18] supports the validity of the Townes-Dailey method for interpreting the changes in nuclear quadrupole coupling constants of XY in terms of electron redistribution when $B\cdots XY$ is formed. The red dots in Figure 8 show a plot $\delta_i(T-D)$ (as obtained from the Townes-Dailey model) against $\delta_i(AIM)$ (as calculated by the atoms-in-molecules method). The result is the straight line through the origin and having the linear regression equation $\delta_i(T-D) = 1.16(3) \delta_i(AIM)$

+0.002(3), with $R^2 = 0.958$. Correspondingly, the open circles shown in Figure 8 are points obtained when $\delta_p(\text{T-D})$ is plotted versus $\delta_p(\text{AIM})$. An excellent straight line through the origin again results, the linear regression equation of which is $\delta_p(\text{T-D}) = 1.20(3) \delta_p(\text{AIM}) + 0.0001(30)$, with $R^2 = 0.975$. Clearly, there is strong correlation between the two methods of obtaining δ_i and δ_p . Numerical values of $\delta_i(\text{AIM})$ and $\delta_p(\text{AIM})$ are given in the Supplementary Information. Similar relationships are found if the NBO charges are used to derive δ_i and δ_p . Numerical values of $\delta_i(\text{NBO})$ and $\delta_p(\text{NBO})$ obtained from the NBO method and their correlation with those from the Townes-Dailey model are given in the Supplementary Information.

It has also been established here that the value of δ_i decreases in an approximately exponential manner as the ionisation energy I_B for removal of an electron from the non-bonding orbital of B or from a π -bonding orbital (when B = HCCH and C₂H₄) increases. Moreover, linear regression fits of the points in graphs of $\ln(\delta_i)$ versus I_B show that the straight-line equations $\ln(\delta_i) = \ln(A) - b(I_B)$ for all but the B \cdots Cl₂ series may be described (see Table 5) in reasonable approximation by $\ln(A) = 1.54(35)$ and $b = 0.376(30) (\text{eV})^{-1}$. Thus, the exponential decay of δ_i with I_B for the five series B \cdots XY (XY = BrCl, Br₂, ICl, IBr and I₂) are only weakly dependent on the nature of the atom, either Br or I of XY, that is involved in the halogen bond. This is also suggested by the straight-line graphs (Figures 2 and 3) that result when $\delta_i(\text{B}\cdots\text{XY})$ is plotted against $\delta_i(\text{B}\cdots\text{X}'\text{Y}')$. Figure 2 shows that $\delta_i(\text{B}\cdots\text{Br}_2) \sim \delta_i(\text{B}\cdots\text{I}_2) > \delta_i(\text{B}\cdots\text{Cl}_2)$ for a given B when B = PH₃ is excluded, while Figure 3 suggests the order $\delta_i(\text{B}\cdots\text{Br}_2) \sim \delta_i(\text{B}\cdots\text{BrCl}) \sim \delta_i(\text{B}\cdots\text{ICl}) \sim \delta_i(\text{B}\cdots\text{IBr}) > \delta_i(\text{B}\cdots\text{I}_2) \gg \delta_i(\text{B}\cdots\text{Cl}_2)$. We note also that the order of δ_i values within a given B \cdots XY series is not correlated with the size of the electric dipole moment of the Lewis base B, as indicated by the larger value of δ_i for complexes in which B is the non-dipolar ethene than for those when B is the highly dipolar molecule HCN.

Finally, a similar treatment of experimental, zero-point nuclear quadrupole coupling constants for the four series B \cdots Cl₂, B \cdots BrCl, B \cdots Br₂ and B \cdots ICl with B = N₂, CO, HCN, H₂O, H₂S, HCCH, C₂H₄, PH₃, NH₃ in which an empirical and incomplete correction was used to compensate for the effect of the zero-point motion of the XY subunits on the coupling constants led to similar conclusions with respect to the exponential decay of δ_i values and of their order for a given B, but somewhat smaller values [28,31]. The smaller values almost certainly from the inadequacy of the zero-point corrections for XY and the neglect of those of B because zero-point oscillations tend to attenuate nuclear quadrupole coupling

constants. The extent of charge transfer in complexes such as those considered here has been calculated by various quantum mechanical approaches by Shaik et al. [7] as part of the debate about polarization versus charge transfer.

5. Conflicts of Interest. There are no conflicts of interest.

6. Acknowledgements

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Table 1 Calculated halogen equilibrium nuclear quadrupole coupling constants for 30 complexes B...Cl₂, B...BrCl and B...Br₂

B...XY	XY = Cl ₂		XY = BrCl		XY = Br ₂	
	$\chi_{zz}^{\text{complex}}(\text{X})/\text{MHz}$	$\chi_{zz}^{\text{complex}}(\text{Y})/\text{MHz}$	$\chi_{zz}^{\text{complex}}(\text{X})/\text{MHz}$	$\chi_{zz}^{\text{complex}}(\text{Y})/\text{MHz}$	$\chi_{zz}^{\text{complex}}(\text{X})/\text{MHz}$	$\chi_{zz}^{\text{complex}}(\text{Y})/\text{MHz}$
N ₂ ...XY	-111.514	-109.471	819.125	-99.515	758.955	738.862
OC...XY	-112.061	-108.134	824.853	-96.605	764.738	721.668
HCN...XY	-113.925	-105.762	842.005	-93.913	781.889	700.169
H ₂ O...XY	-113.735	-106.039	840.039	-94.606	779.734	704.579
H ₂ S...XY	-112.929	-105.437	827.750	-91.977	770.669	689.406
HCCH...XY	-112.241	-106.966	823.407	-95.066	764.883	708.979
C ₂ H ₄ ...XY	-112.370	-104.955	818.171	-90.134	763.146	678.793
H ₃ P...XY	-112.962	-103.520	797.394	-76.837	763.355	627.699
H ₃ N...XY	-116.336	-98.967	855.915	-82.484	800.619	625.275
(CH ₃) ₃ N...XY	-111.475	-73.958	810.630	-66.948	766.272	503.172

Table 2 Calculated halogen equilibrium nuclear quadrupole coupling constants for 30 complexes B...ICl, B...IBr and B...I₂

B...XY	XY = ICl		XY = IBr		XY = I ₂	
	$\chi_{zz}^{\text{complex}}(\text{X})/\text{MHz}$	$\chi_{zz}^{\text{complex}}(\text{Y})/\text{MHz}$	$\chi_{zz}^{\text{complex}}(\text{X})/\text{MHz}$	$\chi_{zz}^{\text{complex}}(\text{Y})/\text{MHz}$	$\chi_{zz}^{\text{complex}}(\text{X})/\text{MHz}$	$\chi_{zz}^{\text{complex}}(\text{Y})/\text{MHz}$
N ₂ ...XY	-2885.642	-83.051	-2699.510	630.729	-2362.614	-2271.021
OC...XY	-2916.267	-77.861	-2733.309	601.675	-2388.927	-2206.256
HCN...XY	-2984.998	-75.496	-2804.080	579.034	-2462.733	-2123.751
H ₂ O...XY	-2968.930	-77.569	-2787.515	591.183	-2448.250	-2146.634
H ₂ S...XY	-2896.604	-74.638	-2730.106	572.232	-2412.259	-2105.063
HCCH...XY	-2892.382	-77.584	-2717.158	593.561	-2389.526	-2164.210
C ₂ H ₄ ...XY	-2839.020	-71.177	-2692.489	552.185	-2392.014	-2063.424
H ₃ P...XY	-2784.449	-62.039	-2671.081	494.492	-2412.415	-1945.076
H ₃ N...XY	-2993.818	-66.014	-2846.873	507.267	-2540.998	-1895.516
(CH ₃) ₃ N...XY	-2844.618	-58.103	-2721.361	442.403	-2486.595	-1648.232

Table 3. Values of free molecule XY and free atom X nuclear quadrupole coupling constants

Dihalogen molecule XY	<i>Ab initio</i> value of $\chi_{zz}^{\text{free}}(\text{X})/\text{MHz}^{\text{a}}$	<i>Ab initio</i> value of $\chi_{zz}^{\text{free}}(\text{Y})/\text{MHz}^{\text{a}}$	Isolated atom X	$\chi^{\text{A}}(\text{X})/\text{MHz}^{\text{b}}$
$^{35}\text{Cl}_2$	-111.059	-111.059	^{35}Cl	-109.74
$^{79}\text{Br}^{35}\text{Cl}$	815.239	-101.956	^{79}Br	769.62
$^{79}\text{Br}_2$	755.281	755.281		
$^{127}\text{I}^{35}\text{Cl}$	-2838.266	-86.216	^{127}I	-2292.44
$^{127}\text{I}^{79}\text{Br}$	-2659.486	653.037		
$^{127}\text{I}_2$	-2326.461	-2326.461		

^aSee Section 2 for details of the level of calculation. ^bValues from atomic spectroscopy (see ref. [26])

Table 4 Intermolecular and intra-halogen electron transfer^a on formation of complexes B...XY

	XY = Cl ₂		XY = BrCl		XY = Br ₂		XY = ICl		XY = IBr		XY = I ₂		Ionisation energy $I_{\text{B}}/\text{eV}^{\text{b}}$
B...XY	$10^2\delta_{\text{i}}$	$10^2\delta_{\text{p}}$	$10^2\delta_{\text{i}}$	$10^2\delta_{\text{p}}$	$10^2\delta_{\text{i}}$	$10^2\delta_{\text{p}}$	$10^2\delta_{\text{i}}$	$10^2\delta_{\text{p}}$	$10^2\delta_{\text{i}}$	$10^2\delta_{\text{p}}$	$10^2\delta_{\text{i}}$	$10^2\delta_{\text{p}}$	
N ₂ ...XY	1.03	1.45	1.72	2.22	1.66	2.13	0.82	2.88	1.15	2.90	0.84	2.42	15.58
OC...XY	1.75	2.67	3.63	4.88	3.14	4.37	4.21	7.61	3.45	6.67	2.52	5.24	14.01
HCN...XY	2.22	4.83	3.85	7.33	3.70	7.16	3.37	9.77	3.31	9.61	2.90	8.84	13.64
H ₂ O...XY	2.14	4.57	3.48	6.70	3.41	6.59	2.18	7.88	2.45	8.04	2.53	7.84	12.62
H ₂ S...XY	3.42	5.12	7.47	9.09	6.56	8.56	8.01	10.55	7.42	10.50	5.91	9.66	10.46
HCCH...XY	2.65	3.73	5.22	6.28	4.77	6.02	5.51	7.87	5.21	7.73	4.33	7.08	11.40
C ₂ H ₄ ...XY	4.37	5.56	10.39	10.77	8.91	9.94	13.67	13.70	11.66	13.10	8.61	11.47	10.51
H ₃ P...XY	5.13	6.87	25.21	22.89	15.53	16.57	24.38	22.03	20.09	20.60	12.89	16.63	9.87
H ₃ N...XY	6.21	11.02	12.46	17.74	11.00	16.89	11.62	18.41	10.76	18.94	9.44	18.80	10.07
(CH ₃) ₃ N...XY	33.43	33.81	32.50	31.90	31.32	32.75	25.34	25.62	24.66	27.36	22.60	29.58	7.85

^a δ_{i} is the fraction of an electron transferred from the Lewis base B to atom X and δ_{p} is the fraction of an electron transferred simultaneously from atom X to atom Y on formation of B...XY.

^bValues of I_{B} are from ref.[27]

Table 5. Parameters of the linear regression fit to $\ln(\delta_i) = \ln(A) - bI_B$ for individual series of complexes $B \cdots XY$

Complex series	Linear regression parameters		
	$\ln(A)$	$b/(\text{eV})^{-1}$	R^2
$B \cdots \text{Cl}_2$	-0.37(38)	0.267(32)	0.910
$B \cdots \text{BrCl}$	1.37(44)	0.352(37)	0.928
$B \cdots \text{Br}_2$	1.23(45)	0.347(48)	0.924
$B \cdots \text{ICl}$	1.89(73)	0.406(61)	0.866
$B \cdots \text{IBr}$	1.57(51)	0.377(42)	0.919
$B \cdots \text{I}_2$	1.64(50)	0.399(42)	0.927
Mean (without $B \cdots \text{Cl}_2$)	1.54 (35)	0.376(30)	

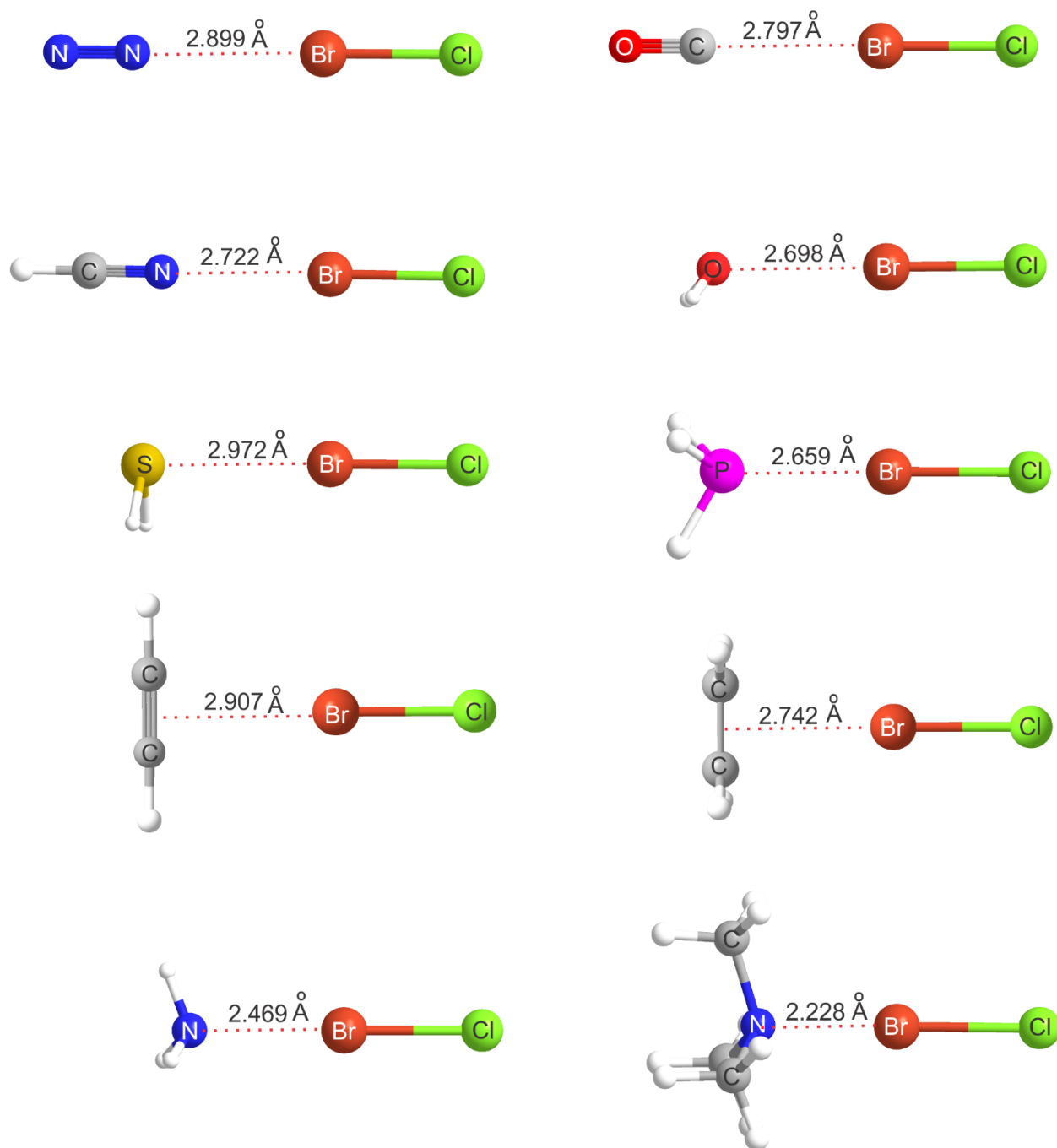


Figure 1. Geometries (drawn to scale) of ten complexes $B \cdots \text{BrCl}$, where $B = \text{N}_2$, CO , HCN , H_2O , H_2S , PH_3 , HCCH , C_2H_4 , NH_3 or $(\text{CH}_3)_3\text{N}$, respectively, optimized at the MP2/aug-cc-pVTZ computational level. The intermolecular bond lengths are given above the red-dotted bonds. Cartesian coordinates for these geometries and those of the $B \cdots \text{XY}$ series having $\text{XY} = \text{Cl}_2$, Br_2 , ICl , IBr and I_2 are available as Supplementary Material.

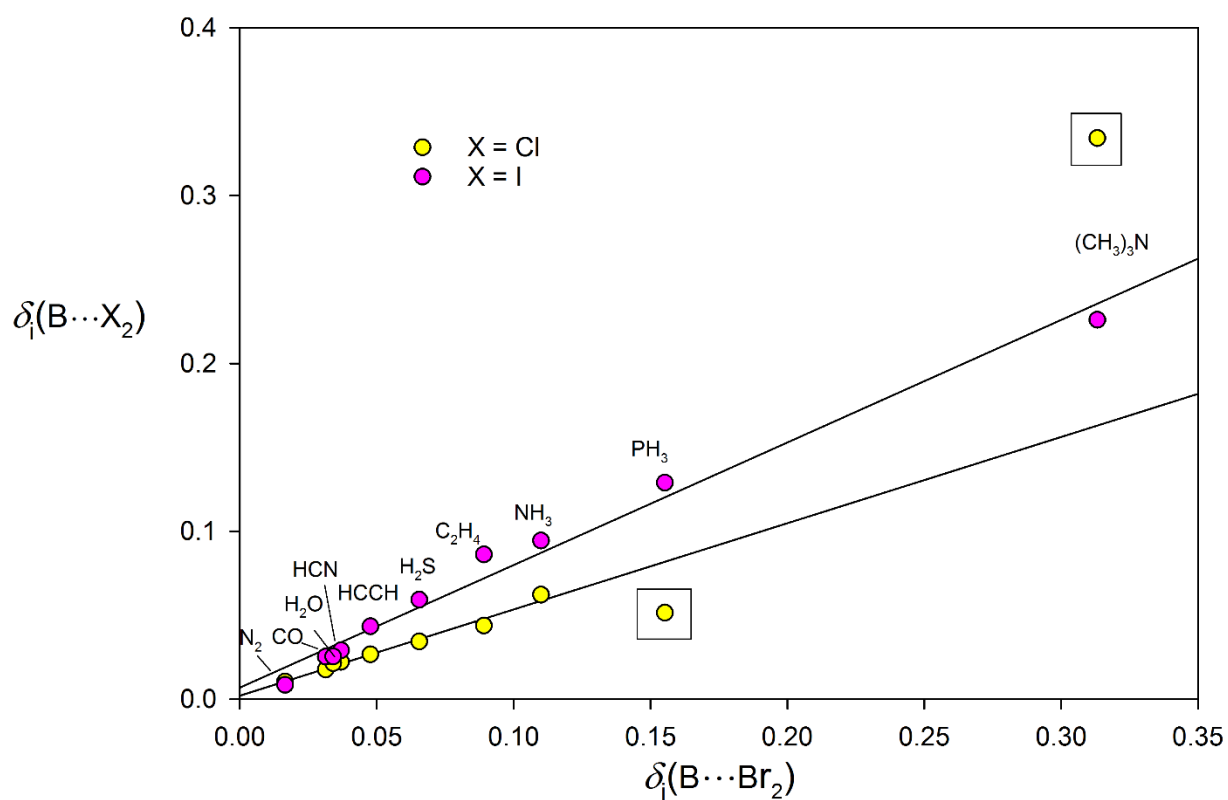


Figure 2. A plot of $\delta_i(\text{B}\cdots\text{Br}_2)$ versus $\delta_i(\text{B}\cdots\text{Cl}_2)$ and $\delta_i(\text{B}\cdots\text{I}_2)$ for the series of complexes $\text{B}\cdots\text{X}_2$. The points in boxes for $\text{H}_3\text{P}\cdots\text{Cl}_2$ and $(\text{CH}_3)_3\text{N}\cdots\text{Cl}_2$ were not included in the linear regression fit to the $\text{B}\cdots\text{Cl}_2$ data, for reasons discussed in the text.

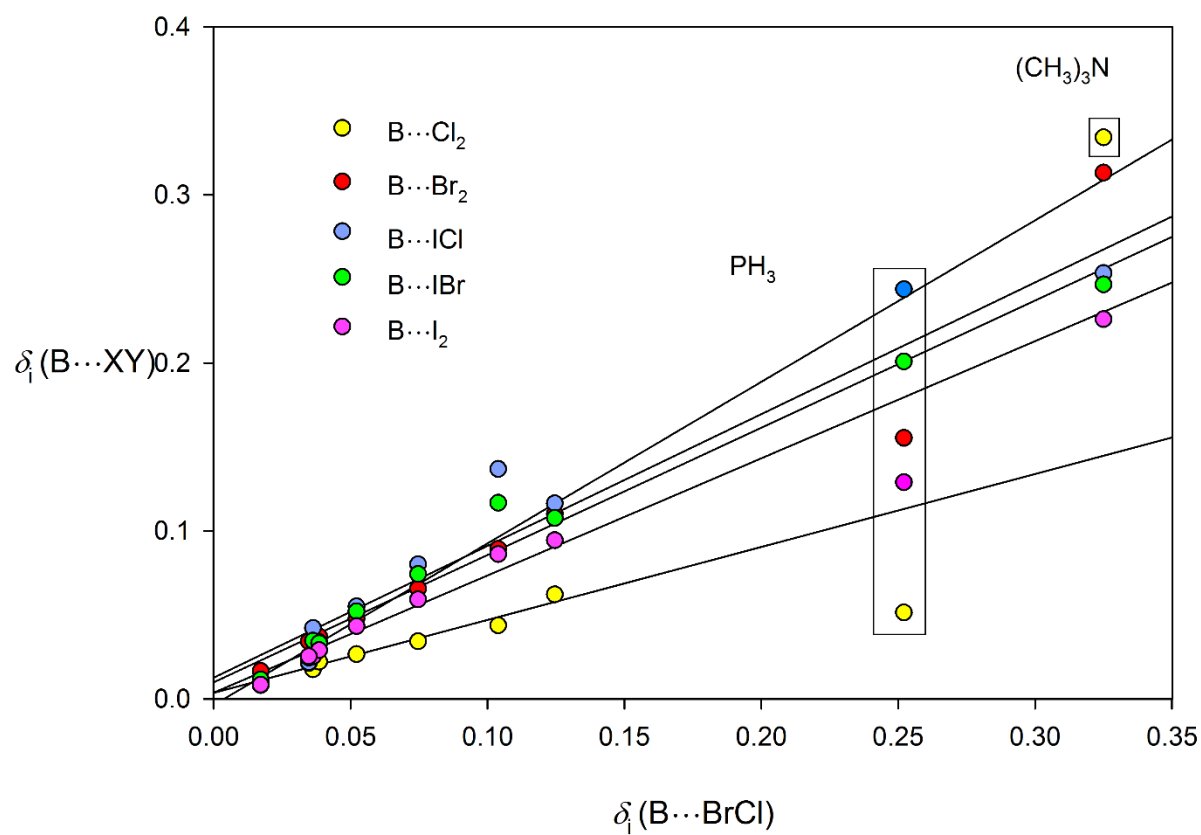


Figure 3. Plots of $\delta_i(\text{B}\cdots\text{BrCl})$ versus $\delta_i(\text{B}\cdots\text{Cl}_2)$, $\delta_i(\text{B}\cdots\text{Br}_2)$, $\delta_i(\text{B}\cdots\text{ICl})$, $\delta_i(\text{B}\cdots\text{IBr})$ and $\delta_i(\text{B}\cdots\text{I}_2)$ for complexes $\text{B}\cdots\text{XY}$. The points in boxes for all $\text{H}_3\text{P}\cdots\text{XY}$ and for $(\text{CH}_3)_3\text{N}\cdots\text{Cl}_2$ were not included in the linear regression fit to the data, for reasons discussed in the text.

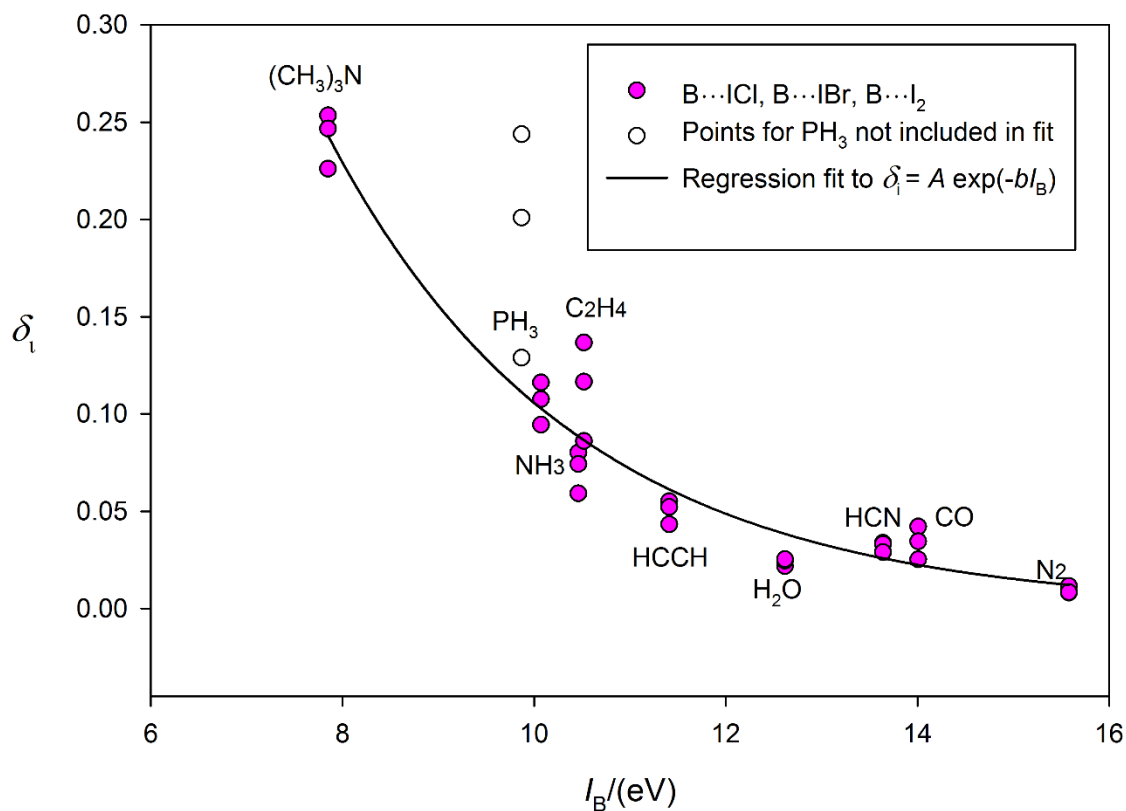


Figure 4. Plot of δ_i versus I_B (the ionisation energy of the Lewis base B) for the three series of complexes $B \cdots \text{ICl}$, $B \cdots \text{IBr}$ and $B \cdots \text{I}_2$, for $B = \text{N}_2$, CO , HCN , H_2O , H_2S , HCCH , C_2H_4 , PH_3 , NH_3 or $(\text{CH}_3)_3\text{N}$. The points for $B = \text{PH}_3$ (open circles) are anomalous in this series (and others, see text) and were excluded from the regression fit to $\delta_i = A \exp(-b/I_B)$, which yielded $A = 5.0(10)$ and $b = 0.387(22) \text{ (eV)}^{-1}$, with $R^2 = 0.944$.

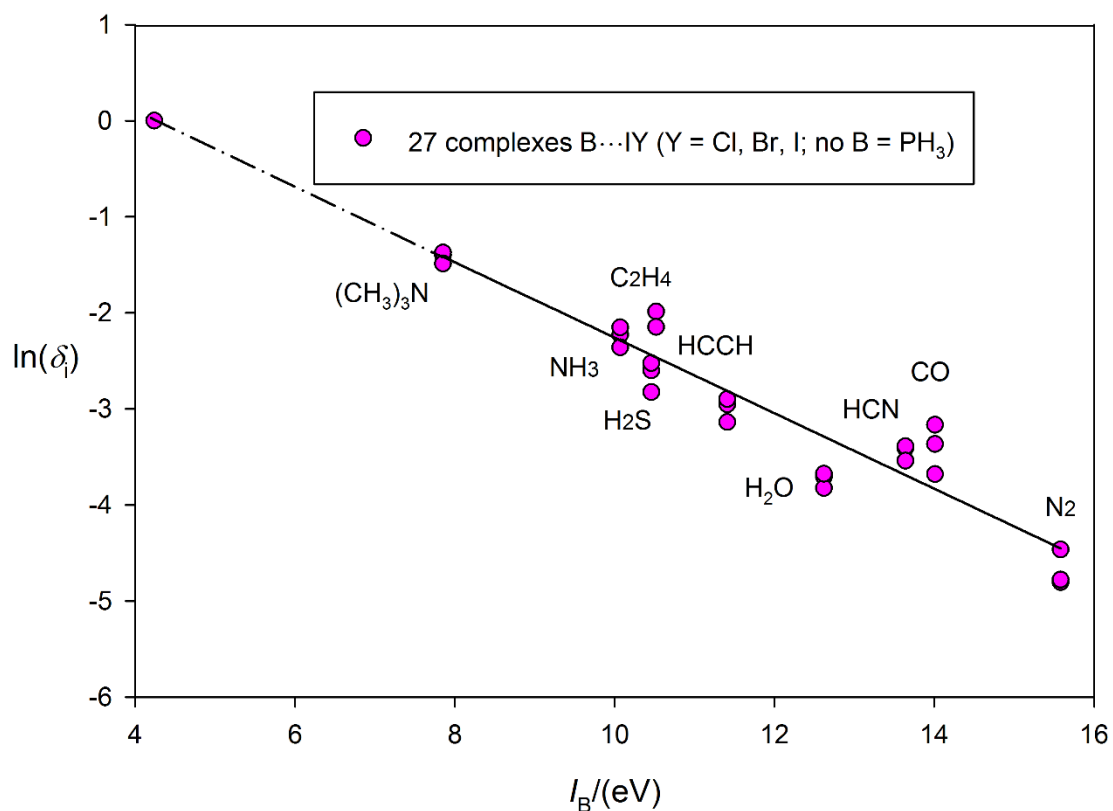


Figure 5. Plot of $\ln(\delta_i)$ versus I_B for 27 complexes $B \cdots IY$ (B as indicated in figure, $Y = \text{Cl, Br and I}$). Note that the points for PH_3 are not included (see text). The solid line is the linear regression fit which is described by the equation $\ln(\delta_i) = 1.67(33) - 0.393(27)I_B$, for which $R^2 = 0.894$. The broken line is the extrapolation of the regression line to the point at which $\ln(\delta_i) = 0$ (therefore $\delta_i = 1$) and $I_B = 4.3(12)$ eV. This point refers to a (hypothetical) Lewis base molecule B of ionisation energy 4.3 eV, for which there would be transfer of a whole electron to I of IY when $B \cdots IY$ is formed.

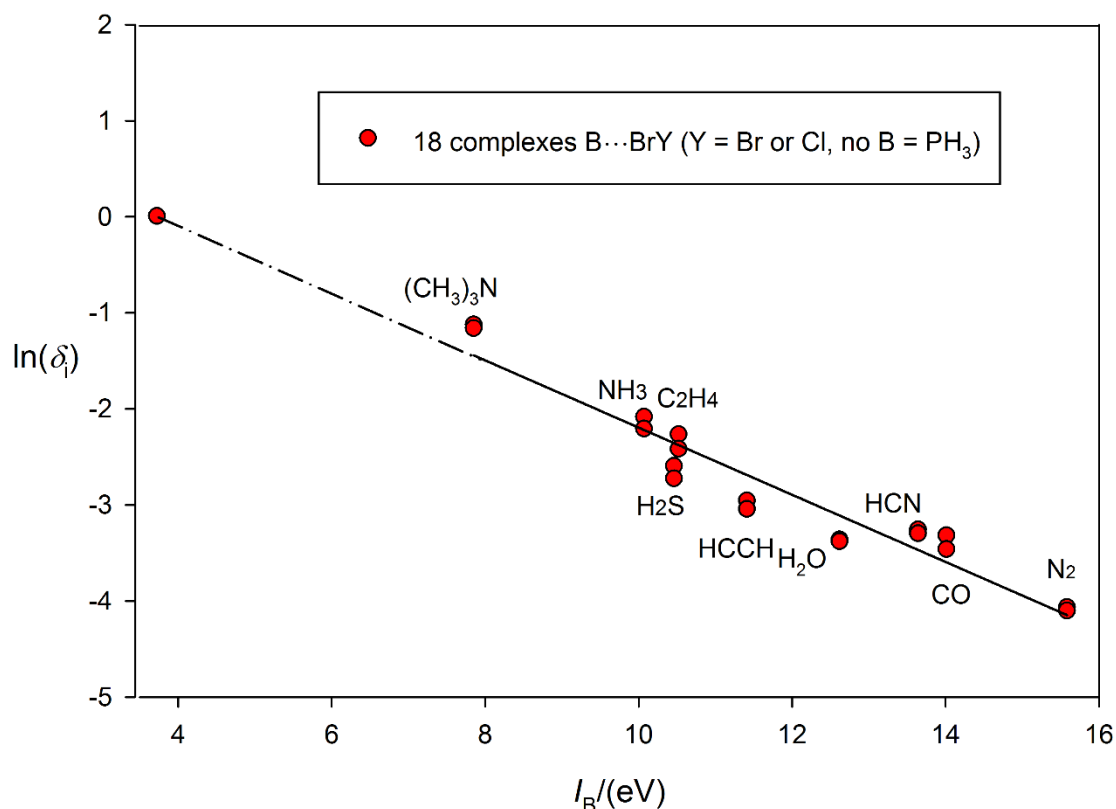


Figure 6. Plot of $\ln(\delta_i)$ versus I_B for 18 complexes $\text{B} \cdots \text{BrY}$ (B as indicated in figure, $\text{Y} = \text{Cl}$ or Br). Note that the points for PH_3 are not included (see text) The solid line is the linear regression fit which is described by the equation $\ln(\delta_i) = 1.30(30) - 0.350(26)(I_B/\text{eV})$, for which $R^2 = 0.924$. The broken line is the extrapolation of the regression fit to the point corresponding to $\ln(\delta_i) = 0$ (therefore $\delta_i = 1$) and $I_B = 3.7(12)$ eV. This point therefore refers to a (hypothetical) Lewis base molecule B of ionisation energy 3.7(12) eV, for which there would be transfer of a whole electron to Br of BrY when $\text{B} \cdots \text{BrY}$ is formed.

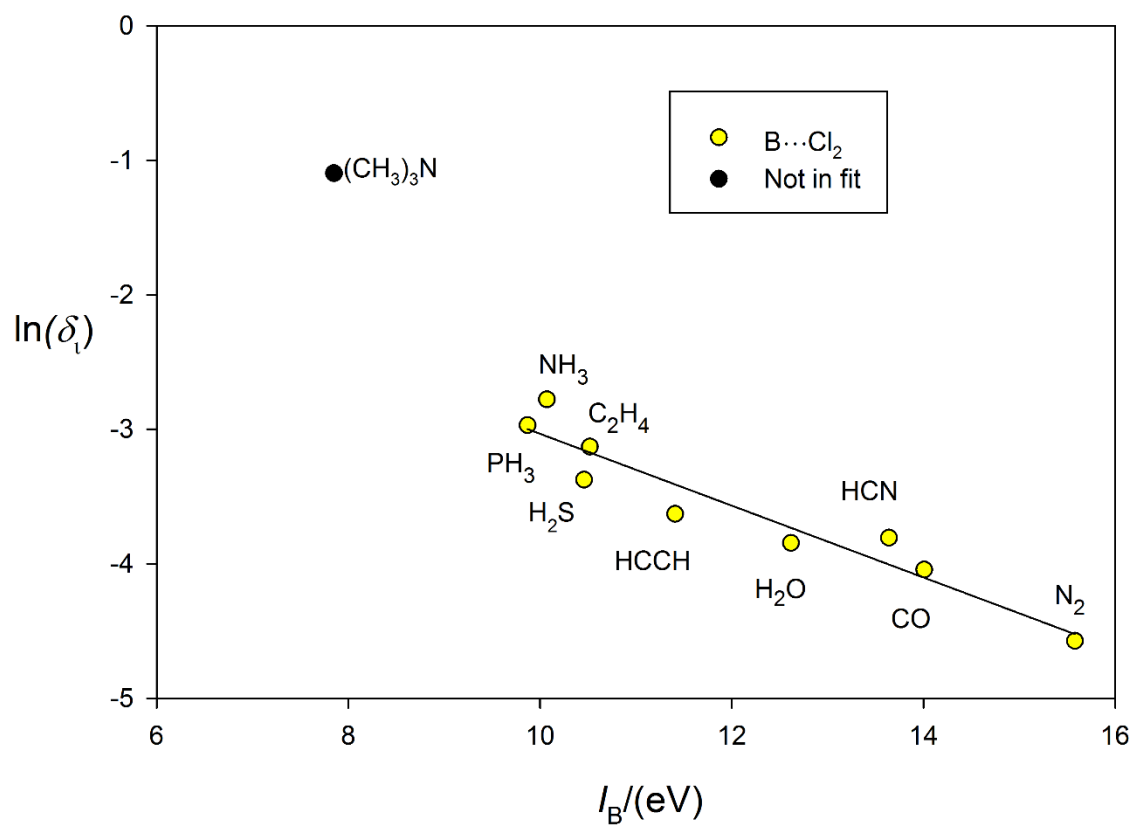


Figure 7. Plot of $\ln(\delta_l)$ versus I_B for 9 complexes $B \cdots \text{Cl}_2$ (B as indicated in the figure). Note that point for $(\text{CH}_3)_3\text{N} \cdots \text{Cl}_2$ is much too high and is not included in the linear regression fit, which is described by the equation $\ln(\delta_l) = -0.37(38) - 0.267(32)(I_B/\text{eV})$, (solid line) and has $R^2 = 0.910$.

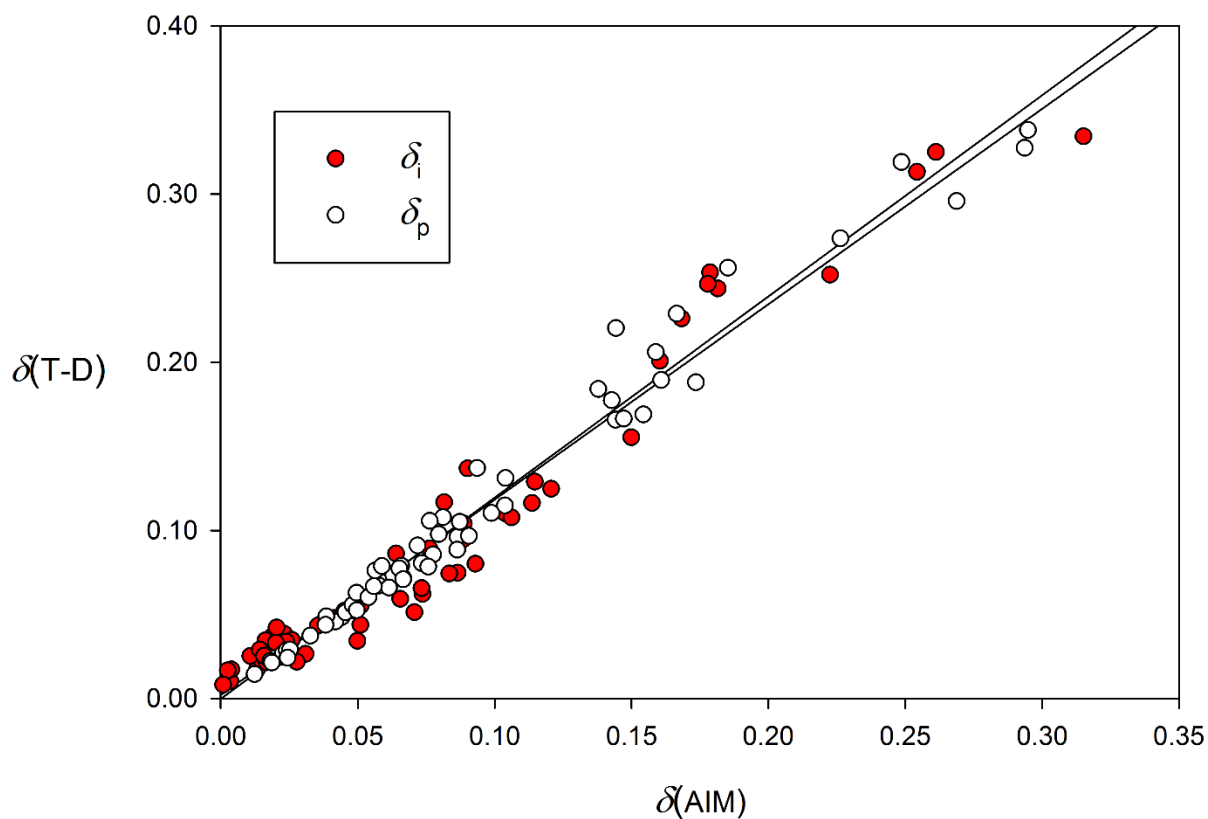


Figure 8. The red-filled circles result when δ_i (T-D) obtained from the Townes-Dailey model for interpreting nuclear quadrupole coupling constants are plotted against $\delta_i(\text{AIM})$ calculated by the atoms-in-molecules methodology. A linear regression fit to the points yields the equation $\delta_i(\text{T-D}) = 1.16(3) \delta_i(\text{AIM}) + 0.002(3)$, with $R^2 = 0.958$. The open circles are obtained from the corresponding plot of δ_p (T-D) against $\delta_p(\text{AIM})$ and lead via linear regression fit to the equation $\delta_p(\text{T-D}) = 1.20(3) \delta_p(\text{AIM}) + 0.0001(30)$, with $R^2 = 0.975$.